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Formation of Easy-to-Recover Polystyrene-*block*-Poly(4-vinylpyridine) Micelles Decorated with Pd Nanoparticles in Solutions of Self-Neutralizing Carbonic Acid

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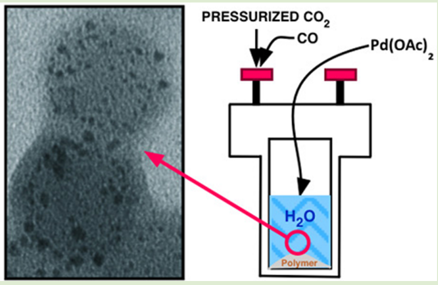
Supporting Information

ABSTRACT: It was found out that block copolymers of polystyrene and poly(4-vinylpyridine) with comparable lengths of blocks could be dissolved in a high-pressure reactor containing water phase saturated with carbon dioxide under high pressure at room temperature. This rather effective dissolution occurs due to a protonation of P4VP nitrogen-containing groups together with a plasticization of the polymer material to be dissolved by a compressed dense CO_2 being contained in the autoclave. The selected block copolymers form rather monodispersed micelles with well-defined and reproducible spherical geometry. They apparently have a hydrophobic polystyrene core and a polycationic poly-4-vinylpyridine corona. The obtained micelles were characterized by various techniques such as DLS, AFM, TEM, and SEM. Further, it was revealed that the corona of such micelles could be decorated with Pd nanoparticles having the diameter around 3 nm.



Nowadays, noble metal nanoparticles (NPs), because of their small size and large surface area, attract huge attention in the advanced science-driven fields like heterogeneous catalysis,[1] surface templating,[2] and so on, allowing to minimize the amount of metal used, which is very beneficial because currently available reserves of noble metals are rather limited.

There are several ways to stabilize metal NPs and to prevent their further growth or aggregation, for example, the usage of polymers, macromolecules of complex geometry, adsorption on a substrate with the affinity for metal NPs, and their incorporation in polymeric micelles.[1,3] It is well-known that metal NPs stabilized in the corona of the micelles can serve as highly active, stable, and renewable catalysts for chemical engineering.[4−8] It is important to mention that, when NPs are localized in the corona of such micelles, they remain accessible for reagents, whereas in the case of NPs encapsulated in a micelle core, the accessibility may be limited and thus the catalytic activity may be impaired.[6]

There are two conventional methods for the preparation of micelles from polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) copolymers. According to the first approach, one initially dissolves the copolymer in a good solvent for the polymers of both blocks.[7−20] Then a selective solvent for one of the blocks is added drop by drop in the initial solution. This results in the formation of micelles with either a polystyrene (PS) core and a poly(4-vinylpyridine) (P4VP) corona[7,9−15] or vice versa.[9,16] After that it is necessary to perform a dialysis in order to remove the solvent of the first type.[7,9,13,14] Another approach to obtain micelles with a PS shell and a P4VP core is to dissolve the copolymer in the selective solvent for PS at around 90 °C.[17−23] Elevated temperature is required in order to break intermolecular bonds of the glassy polymer material.[24]

On the contrary, we propose more environmentally benign approach to form micelles from this copolymer in the solutions in water saturated with carbon dioxide under high pressure, that is, in the solutions of carbonic acid at room temperature. Usually for chemical reactions with conventional acids (even with environmentally friendly ones) as reaction media it is necessary to perform at the end neutralization and utilization of salts. These salts are to be considered as hazardous waste and thus utilized properly if any reagents, products, intermediates or potential side products are considered hazardous ones. On the contrary, carbonic acid is absolutely eco-friendly, nontoxic, easy-to-form from easily available H_2O and CO_2, and self-neutralizing at decompression medium. Indeed, there is no need to perform any time-consuming postreaction neutralization and salt disposal or recovery, because carbonic acid is completely autoeliminated upon depressurization of CO_2 after reaction, as far as it decomposes spontaneously into gas carbon dioxide and pure water.

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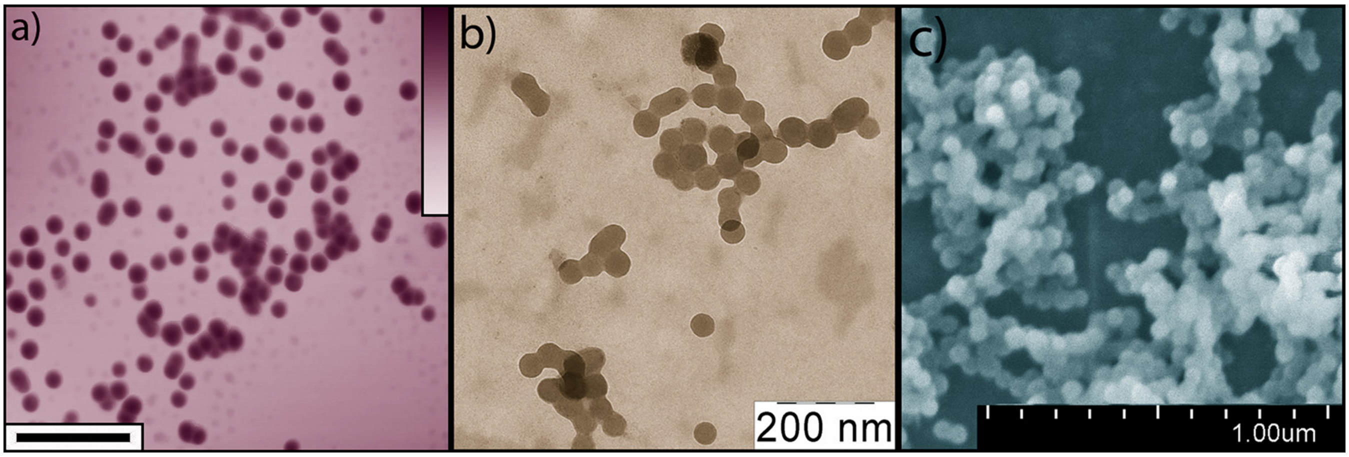


Figure 1. Microphotographs of the pristine PS150-*b*-P4VP110 micelles, adsorbed from the solutions in carbonic acid (pH = 2.8, copolymer concentration 0.16 g/L) as resolved from (a) AFM, mica as a substrate, scan size 2 × 2 μm, scale bar 500 nm, and height scale 100 nm; (b) TEM, S160 as a substrate, scan size 0.9 × 0.9 μm; and (c) SEM, S160 as a substrate, scan size 1.7 × 2.5 μm.

As opposite to the basic approaches discussed above we eliminate completely any usage of any organic presolvent. Thus, the reaction mixture contains no traces of any organic residual solvent without any purification applied. It seems to be rather advantageous, because such residual organic solvent can cause undesirable side reactions or poison the catalyst. The process proceeds at room temperature, thus, elevated temperature is not required either. It should be noted that the increase in the temperature decreases the solubility of CO_2 in water.[25] Consequently, one can expect the corresponding increase of the pH of the media, which deteriorates solubility of the block copolymer.

In the present work we demonstrate that in the acidic conditions of the solutions of carbonic acid one can construct micelles from the block copolymer and localize metal NPs in their corona for subsequent usage as renewable catalysts.

Figure 1 shows the AFM, TEM, and SEM images of the pristine PS-*b*-P4VP block copolymer micelles as adsorbed from the solutions in carbonic acid at the substrates surfaces at room temperature. It can be noticed that the micelles have regular spherical geometry. The aggregation tendency observed on the substrates is due to the surface-tension-driven effects at the solvent evaporation step. The radii of the visualized pristine micelles were around 30 nm. For the discussion on the sizes of the micelles, see Supporting Information.

Apparently, during the process of the dissolution in the solutions of carbonic acid, first of all, the plasticization of PS block by high pressure CO_2 at room temperature occurs. Indeed, it is well-known that CO_2 compressed under high pressure with a density close to 1 mg/mL is a plasticizer for PS.[26−28] The plasticization of P4VP may also take place.[29] Second, the protonation and the subsequent dissolution of P4VP occurs in acidic medium of the solutions of carbonic acid (pH is around 2.8[30,31]). This effect is similar to that described earlier for the protonation and dissolution of nitrogen-containing chitosan macromolecules in carbonic acid.[32−36] Therefore, during the exposition in a high-pressure reactor at the conditions of a highly mobile mixture of water, dissolved CO_2, and plasticized block copolymer macromolecules, the processes of the self-assembly of the block copolymer into the micelles proceed faster than in the case of conventional solvent at room temperatures. Therefore, one can suppose that at this stage micelles exchange with macromolecules very intensively and reach equilibrium comparably fast even at room temperature. Obviously, micelles that are formed in the solutions of carbonic acid have the P4VP corona and the PS core, in which PS is plasticized during the exposition in the closed high-pressure reactor. But after the decompression of the reactor, CO_2 is eliminated from aqueous media, and thus, PS undergoes a reverse process of vitrification, which is the factor of the additional stabilization of the formed micelles.

After the decompression, CO_2 goes out of water and, as a consequence, pH of the medium raises slowly up to the value 5.5. But the micelles do not loose their solubility yet. This fact was demonstrated by the DLS (the obtained size of the micelles in the solution correlates rather well with the results of the visualization of the micelles on the substrate by several methods of high resolution microscopy, if one takes into account the effect of collapse of the corona due to the removal of the solvent). In our complex system of copolymer−carbonic acid−micelles−water, some hysteresis of the block copolymer solubility exists. Indeed, at pH = 5 previously assembled micelles do not precipitate, but at these conditions the dissolution of the initial copolymer is not observed yet. Moreover, by bubbling the solution with N_2, followed by a centrifugation, one can easily remove the micelles from the solution, but their subsequent dispergation in the solutions of carbonic acid leads to a complete restoring of all properties of the micelles without any aggregation.

Taking these facts into account, the well-known in the literature procedure of the usage of such micelles as substrates for immobilization and stabilization of metal catalytic nanoparticles was considered promising to implement.[8,37,38] With such a scheme the NPs are localized not in the core, but in the corona of the micelles, so the access of reagents and removal of products of the reaction is not hindered. But at the same time, steric repulsion of coronae of different micelles, formed by the soluble in the solutions of carbonic acid P4VP block, prevents NPs from the aggregation and precipitation.

We chose palladium acetate $Pd(OAc)_2$ as a metal precursor. It is soluble in aqueous media of the solutions of carbonic acid and form complexes with the P4VP block in the corona of the micelles. This precursor was subsequently reduced during the process of a saturation of the reactor with carbon monoxide. As a result, we obtained palladium nanoparticles (PdNPs) with the mean diameter of about 3 nm, localized in the corona of the micelles (see Figure 2a). Microanalysis in the SEM experiment confirms a presence of metal Pd inside the micelles, which is also indirectly confirmed by the essential raise of the contrast of the micelles in the SEM microphotographs in comparison with the initial pristine micelles that are not decorated with metal (see Figure 2b).

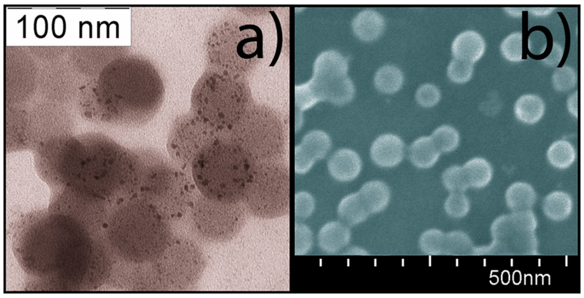


Figure 2. EM microphotographs of PS-*b*-P4VP micelles decorated with PdNPs localized in the P4VP corona: (a) TEM, (b) SEM.

The obtained solutions of the micelles decorated with the metal NPs can serve as active, stable, and renewable catalysts for chemical reactions, as far as we showed that one can remove the micelles from the solution, separate the synthesized product, and dispergate the micelles again in carbonic acid for a subsequent new synthesis. The important advantage of this system is a spontaneous decomposition of carbonic acid into CO_2 and H_2O; therefore, it is not required to neutralize it or to do some subsequent washing of the synthesized product from any salts or acids. The applications of this system for the real catalytic reactions are to be discussed in a more detailed publication we plan to prepare later on.

■ EXPERIMENT SECTION

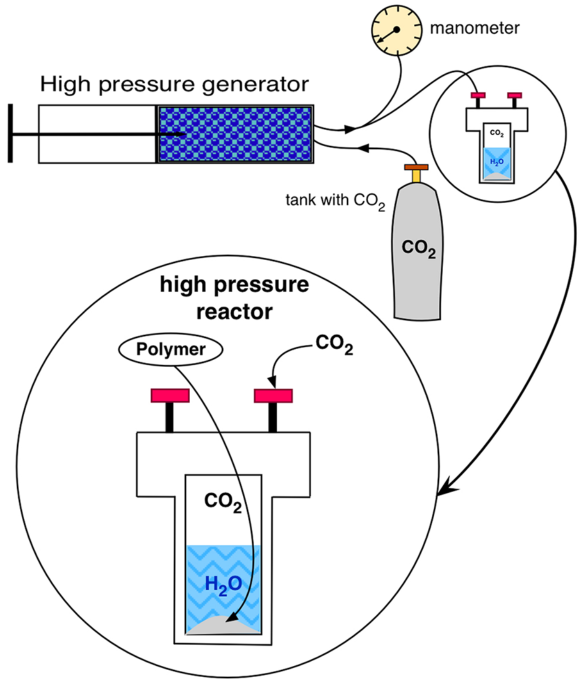
We used a copolymer PS150-*b*-P4VP110 purchased from Polymer Source, Inc., Canada. In the experiments we utilized CO_2 of high purity (>99.997%, Linde Gas Rus, Russia) to saturate water and thus generate solutions of carbonic acid. We used water purified on the Millipore Milli-Q Synthesis system.

The self-organization of the PS-*b*-P4VP copolymer in water saturated with CO_2 under high pressure was performed as follows. We put 1 mg of the copolymer powder and 5 mL of freshly prepared Milli-Q water in the reactor with the total volume of 10 mL. Further, we tightened the reactor, injected liquid CO_2 by raising the pressure up to the 30 MPa at room temperature (25 °C; see Scheme 1).

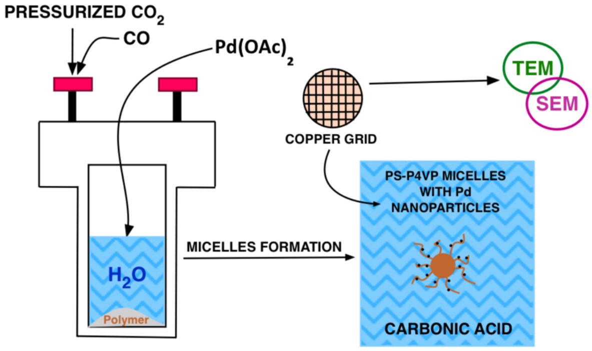
High pressure is required in order to ensure reasonably high concentration of micelles (i.e., catalysts when the micelles are decorated with metal) for the real applications. At such conditions the water phase inside the pressurized reactor slowly became acidic (pH = 2.8), and amino groups of P4VP blocks protonate in the presence of carbonic acid, thus, as a result, P4VP becomes soluble in the aqueous solution, while PS remains hydrophobic and tries to hide itself from the solvent. This is achieved via micelle formation. It should be noted that simple bubbling of the water phase with CO_2 provides the pH value of about 4. At these conditions, the dissolution of the copolymer in reasonable quantities is not detected yet. We performed an exposition (i.e., dissolution and micelles formation) during several days in order to obtain well-defined, regular spherical shaped, and monodisperse micelles. The exposition was ended at room temperature by means of a rather slow decompression.

The scheme of the experiment with PdNPs (see Scheme 2) is similar to the previous one. After the formation of the PS-*b*-P4VP micelles for several days, as described above, the high-pressure reactor was opened and 0.1 mg of palladium acetate was added to the solution of micelles. After that the autoclave was closed and pressurized with CO_2 up to 30 MPa again. The localization of $Pd(OAC)_2$ inside the micelles coronae was achieved during several days. Then the autoclave was depressurized again, at first it was purged with carbon monoxide (1 MPa) and then it was pressurized back with CO_2 up to 30 MPa. The reduction of palladium acetate with carbon monoxide was performed in the CO + CO_2 atmosphere during 1 day.

Scheme 1. Scheme of the Experimental Equipment



Scheme 2. Scheme of the Formation of the PS-*b*-P4VP Micelles with Encapsulated PdNPs



The direct characterization of the morphology of the micelles was performed by different methods that are atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and dynamic light scattering (DLS). For other details on characterization, see Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The discussion on the catalytic activity, on the micelles sizes, and some details on the characterization of the micelles. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00281.

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Notes

The authors declare no competing financial interest.

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